IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Joachim Hossick-Schott	Examiner:	Ha, Nguyen T.
Serial No.	10/692,649	Group Art:	2831
Filing Date:	October 23, 2003	Docket No.:	P0010579.00
Title:	ADVANCED VALVE METAL ANODES WITH COMPLEX INTERIOR AND SURFACE FEATURES AND METHODS FOR PROCESSING SAME		

DECLARATION UNDER 37 C.F.R. § 1.131 ANTEDATING A REFERENCE

I hereby declare the following:

1) I am currently and correctly named as an inventor in the pending patent application entitled "ADVANCED VALVE METAL ANODES WITH COMPLEX INTERIOR AND SURFACE FEATURES AND METHODS FOR PROCESSING SAME", U.S. patent application serial number 10/692,649.

2) The invention disclosed within the above-referenced patent application was conceived of by me and the other named inventors before May 30, 2003.

3) An Invention Disclosure Form was completed that described the invention and was submitted to the Medtronic, Inc. legal department for consideration before May 30, 2003 (a redacted copy of said form is attached hereto).

4) I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: 17 July 07

Anthony W. Rorvick

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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Date: July 17, 2007

Joachim Hossick-Schott

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Date: 12 July 2007

Steven J. May

Steve Joseph May

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Joachim Hossick-Schott	Examiner:	Ha, Nguyen T.
Serial No.	10/692,649	Group Art:	2831
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Date: 3/16/07

John D. Norton

McClellan, Molly Malka

From: McClellan, Molly Malka
Sent: Thursday, June 28, 2007 11:37 AM
To: Hossick-Schott, Joachim; May, Steve; Norton, John; Rorvick, Anthony
Subject: Please sign declaration for P10579.00

Importance: High

Attachments: Hossick-Schott Dec Under 1.131.pdf; May Dec Under 1.131.pdf; Norton Dec Under 1.131.pdf; Rorvick Dec Under 1.131.pdf

Title: ADVANCED VALVE METAL ANODES WITH COMPLEX INTERIOR AND SURFACE FEATURES AND METHODS FOR PROCESSING SAME
Filed: 10/23/2003

Dear Inventors,

We are in need of a declaration from you for purposes of prosecution of this patent application, on which you are listed as an inventor. A copy is attached. Please print the one with your name on it, sign it and return it to me via mail. Any questions may be directed to the attorney on this matter, Carol Barry, at (763) 513-4673, or by way of response to this email.

Thanks,

Molly "Malka" McClellan
Medtronic CRDM Legal Team
Patent Legal Assistant to:
Girma Wolde-Michael
Carol F. Barry
7000 Central Avenue NE, Mail Stop T160
Minneapolis, MN 55432
Phone: (763) 514-6662
Fax: (763) 514-6982


Hossick-Schott Dec Under 1.131.pdf (51 KB


May Dec Under 1.131.pdf (5


Norton Dec Under 1.131.pdf (5


Rorvick Dec Under 1.131.pdf (

DISCLOSURE FILE

*10579.00 Attorney: GWM Division: LP003

Title: WET ELECTROLYTIC VALVE METAL ANODES INCORPORATING A TUNNEL OR CHANNEL ARRAY

Inventors: Kossick-Schott, Joachim
May, Steve J.
Norton, John D.
Norvick, Anthony W.

Status: O Submitted Date: Last Reviewed:
Substatus: REV Approved to File Next Review: (

Related ID:

Outside Counsel:

Licensee: License File No.:

Other Information:

Minutes:

P 10579.00

Medtronic

INVENTION DISCLOSURE FORM

Please fill out this form as completely as possible. If the allotted space is not sufficient, use a separate sheet. Have your manager sign the form and forward it to the Patent Section of the Law Department. Please attach any drawings and technical descriptions that are available and assemble copies of the background articles, books, advertisements, etc., for use by your patent attorney. For a copy of this form on diskette or for information on network retrieval of this form, please call Systems Support at ext. 4111.

1. Inventor(s) Full name(s)	Mail Stop	Home Address (include Zip Code)
Joachim Hossick Schott	H136	5330 DuPont Avenue South, Minneapolis, MN 55419
Steve May	H136	5937 Vine Hill Road, Minnetonka, MN 55345
John D. Norton	H136	2153 Violet Lane, New Brighton, MN 55112
Anthony Rorvick	H136	10641 Shady Oak Court N, Champlin, MN 55316

2. Title of Invention: Wet Electrolytic Valve Metal Anodes Incorporating a Tunnel or Channel Array

3. How have others addressed this problem (List and attach any patents, books, articles, devices, Medtronic or competitor's products, ... other backgrou... materials you used or wi... prior art)?

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d.) Using the cathode rods as alignment posts during manufacture.
US # 5,801,917, US 5,908,151 and 5,983,472 (Pacesetter) and US #5,522,851 (Ventritex) talk about 2 alignment holes punched through the anode foil and US # 6,275729 does talk about at least three larger holes, one of which is, for reasons not obvious to the reader, not supposed to be used, for the purpose of inserting a mounting member into the holes. The present invention teaches the insertion of cathode into the hole, which may have the additional side benefit of aiding the alignment of the anode during the manufacture of the capacitor. Thus, it is believed that the present invention's intent is entirely different from what is taught is US #6,275729, US # 5,801,917, US 5,908,151 and 5,983,472.

4. The invention is described on pages 63-64 of Lab Notebook No. 8001, 49-50 of Lab Notebook No. 8197, and 90-95 and 99-100 of Lab Notebook No. 10310 (Please ar

5. When was a device built which included the invent

Who built it? Joachim Hossick Schott Where is it? MECC North Building, Capacitor Research Lab

Who has supporting documents? Joachim Hossick Schott

Who witnessed tests? Capacitor Research Group When and where? Dec 20, 2001, MECC North Building, Capacitor Research Lab

6. Discuss the problems which the invention is designed to solve, referring to any prior devices of a similar nature with which you may be familiar.

Many types of electrolytic capacitors use anodized valve metals for their anode materials. Two methods are frequently used to increase the active surface area of the anode and the corresponding capacitor energy density. The first method consists of producing the anode by pressing a powder of the valve metal into a porous slug, sintering the slug, and subsequently anodizing the slug to form the active dielectric oxide. This method is frequently used for, but not limited to, Tantalum and Niobium electrolytic capacitors. The second method consists of electrochemically etching a thin foil of the valve metal to create a network of tunnels and subsequently anodizing the foil to form the active dielectric oxide. The foils are then stacked in layers to form anode elements. This method is frequently used for, but not limited to, Aluminum and Tantalum electrolytic capacitors. In each case, the network of pores in the resulting anode materials greatly impacts mass transport to and from the active anodic oxide. This may impact capacitor performance in two significant ways. The present invention improves capacitor performance by minimizing those impacts.

First, attempting to anodize valve metals, specifically Tantalum and Niobium, in the form of pressed and sintered powder electrodes at high voltages (> 200 V) frequently results in the failure of the samples during anodization because of thermal energy dissipated within the porous electrode structure. Therefore, the extremely hot and possibly chemically cracked electrolyte within the pores of the structures needs to be replenished with cool, fresh electrolyte from the reservoir. If, in an effort to increase the active energy density of the capacitor, anode thickness is increased and/or the anode porosity is altered, electrolyte replenishment is impeded. This may be offset by introducing an array of through-holes or channels into the anode to allow for electrolyte flow during the formation process.

Second, for both sintered slug and etched foil anodes, the porous electrode structure restricts movement of ions within the electrolyte necessary to complete the circuit between the anode and cathode. As a result, the equivalent series resistance (ESR) of the capacitor will increase if the anode thickness is increased and/or the anode porosity is altered in an attempt to increase the active energy density of the capacitor. Introduction of an array of through-holes or channels in the face or the side of the anode slug or stack will improve the ESR.

Further ESR improvements for Ta, Nb and Al anodes (the former two in the form of sintered slugs and the latter in the form of a slug composed of individual, anodized Al foil members, all with an array of through-holes either on the face or on the side of the anode) will come from inserting cathode wire coated with a thin layer (approximately

10 micron, actual thickness depending upon the hole diameter) of a high capacitance material such as RuO2 or IrO2 or NiO2 or the like. The cathode wire will be wrapped with tubular sack of polymeric separator and inserted into the holes. The cathode wires are connected to the cathode terminal, which may either be the case of the capacitor or a separate cathode feedthrough wire. No prior art is known is this area. In addition, the cathode wires may be used as guide posts during production of Al, Ta or Nb anodes if they are welded to one part of the case prior to the assembly of the capacitor. Anodes then would be simply dropped into the cathode post array and the alignment of the anode to the case is significantly improved and simplified.

7. State the advantages of the invention over presently-known devices, systems or processes.

Clearly, the presently suggested method of anode preparation saves valuable formation time when compared to the known methods of anode preparation and will certainly increase yield during formation simply because the exchange of electrolyte is improved. Lab experiments have shown that Ta anodes with a tunnel array can be formed to 275 V in about 30 hours as opposed to formation times as high as 100+ hours in the case of anodes without the hole array, especially when the anode with the tunnel array is formed with the pulsed formation potential method disclosed earlier. In addition, lab experiments have shown that the ESR of the finished capacitor will go down by approximately 50% for anodes with the hole array vs those without

The ESR is expected to further improve when the hole array is filled with cathode wire composed of a substrate wire such as Ru or Ti and coated with a thin layer of high capacitance metal oxide, e.g., RuO2, IrO2, NiO2 or the like. The rods may also consist of etched, porous and nested Aluminum tubes, whereby an outer tube encloses one or several inner tubes in the fashion of Russian wood dolls in order to maximize surface area. The cathode wires prepared in this way, i.e., consisting of metal oxide coated cores or consisting of nested tubes, and separated from the anode with a thin polymeric separator may also favorably be used as guide posts for the insertion of Al anode plates, thereby simplifying the production of Al capacitors. Specifically, Medtronic may also benefit from this invention as it may enable Medtronic to utilize RuO2 and other high capacitance metal oxides as cathode materials in conjunction with Al, Ta and Nb anodes as an alternative to what is proposed in the patents of Evans (e.g., US# 5,369,547 "Capacitor" (1994) and US 5,469,325 "Capacitor" (1995) and US# 5,559,667, wherein RuO2 and other metal oxide are patented as a cathode material to be coated on the case of the capacitor). This invention substantially inserts the cathode into the anode slug. The cathode wires may then be connected to the case or they may be connected to a separate cathode feedthrough wire. As a side effect in the case of flat Al capacitors, this invention may save valuable capacitor volume because the number of cathode sheets and separator sheets may be reduced or they may not be needed at all.

8. List all known and other possible uses for the invention.

Formation of Tantalum and Niobium sintered powder anodes, operation of sintered Ta and Nb sintered powder anodes, manufacture of capacitors with sintered Ta and Nb or capacitors with stacked Al foil plates, operation of capacitors with sintered Ta and Nb or capacitors with stacked Al foil plates.

9. Specifically describe the invention and its operation. You may use and attach copies of sketches, prints, photographs and illustrations which should be signed, witnessed and dated. Use numbers and descriptive names in descriptions and drawings.

An array of holes in the anode composed of Ta or Nb will shorten the formation time of these anodes drastically. At the same time, the volume of the anode is reduced only by a small amount, approximately 5%, and this volume reduction may actually not be noticeable in terms of a capacitance loss since the electrolyte access to the volume of the anode is improved. The hole array may be introduced at the time of pressing the anode. In the case of stacked anodized Aluminum plates, the holes may be drilled or die-cut at the time of die-cutting the individual Al plates. The ESR of Ta capacitors with the hole array does improve by about 50 %. The ESR of an Al slug composed of individual anodized Al plates is likely to improve, too. The ESR of Ta, Nb and Al caps will go down further if cathode wires coated with a high capacitance material such as RuO2 or other suitable metal oxides are

inserted into the holes, of course with a proper polymeric separator between anode and cathode, e.g., a tubular sack made from GORE separator material (see sketches on lab book pages 99-100).

10. List all features of the invention that are believed to be novel.

A. Introduction of an array of holes into valve metal anode slugs, consisting specifically of Ta, Nb and Ta/Nb alloyed sintered powders, to reduce formation time and improve formation yield (Hossick Schott).
B. Introduction of an array of holes into valve metal anode slugs, consisting specifically of Ta, Nb and Ta/Nb alloyed sintered powders, to improve ESR (Norton, Hossick Schott).
C. When using two or more anode slugs connected in parallel and in physical contact, pressing channels, grids, arrays of channel, etc into the surface of the slug prior to sintering or otherwise modifying the surface to promote electrolyte access between the slugs. (Norton)
D. When using two or more anode slugs connected in parallel and in physical contact, periodically placing a more porous slug in the stack to increase electrolyte access. (Norton)
E. Introduction of high capacitance cathode wire(s) into the tunnel array to further improve ESR. (Hossick Schott)
F. Introduction of high capacitance cathode wire(s) into the tunnel array to ease placement / alignment of the anode during production of the capacitor. (May, Hossick Schott)
G. Using high capacitance, metal oxide coated wires as the inserted cathode material and connecting the cathode wires to either a separate cathode feedthrough wire or directly to the case of the capacitor. (Hossick Schott)
H. Orienting the anode plates perpendicular to the cathode plates, rather than parallel to the cathode plates, in a stacked plate capacitor to increase electrolyte access. (Norton, Rorvick)
I. In a stacked plate capacitor in which the anode and cathode plates are perpendicular, periodically placing a porous separator or other material between anode plates to increase electrolyte access. (Norton)
J. In a stacked plate capacitor in which the anode and cathode plates are perpendicular, periodically placing a more thoroughly etched and more porous foil in the stack to increase electrolyte access. (Norton)
K. In a stacked plate capacitor in which the anode and cathode plates are perpendicular, intentionally increase the extent of etching in the anode foil in parallel with the foil surface. (Norton)
L. In a stacked plate capacitor in which the anode plates have through holes and an inserted cathode in the through hole, whereby the acthode consists of nested Aluminum tubes. (May)

11. Sale or Publication (Needed to establish the date of any printed publication, public use or sale, since no U.S. patent application may be filed after one year from such date.)

a. If a device has been offered, or will be offered for sale, or used for profit or otherwise publicly disclosed--state when and to whom delivered and how used?

N/A

b. Has a printed description of this invention been made available to persons outside the company? How and when and was use restricted? (e.g., licensing agreement, non-disclosure agreement, [illegible] legends, etc.)

N/A

12. Inventor(s) Signature(s) (REQUIRED):

Steven J. May

Manager's Comments

How is this invention important to your products, plans or goals?

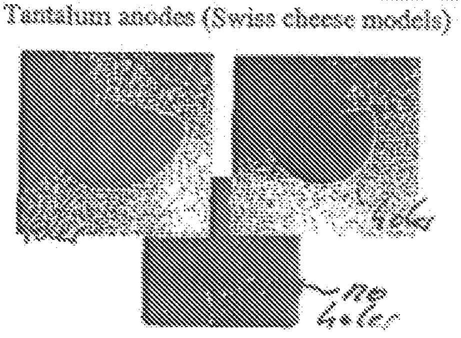
Manager's Signature (REQUIRED) _____ Date _____

(Manager: Please forward to Patent Section of Law Department upon completion of your review.)

From Page No.

I have had not much luck forming the thicker slugs, i.e., the ones about ~7 mm thick. They all, or almost all, failed, only one or two made it to a forming voltage of 225 V. Therefore, I came up with the idea of drilling holes into the slug, ideally through the side, and ideally right after pressing. Since I now have sintered slugs, I have to use a hard drill (W carbide), and, for small holes ≤ Ø 1.0 mm, only short flute length < 20 mm are available. Therefore, I drilled through the face of the slugs, using a Ø = 0.70 mm W carbide drills. The improvement in my ability to form these anodes with the holes is stunning: all ones with the hole pattern in them were formed to ~200 V or 225 V without

Tantalum anodes (Swiss cheese models)



Witnessed & Understood by me: [signature] 7630

Invented by: [signature]

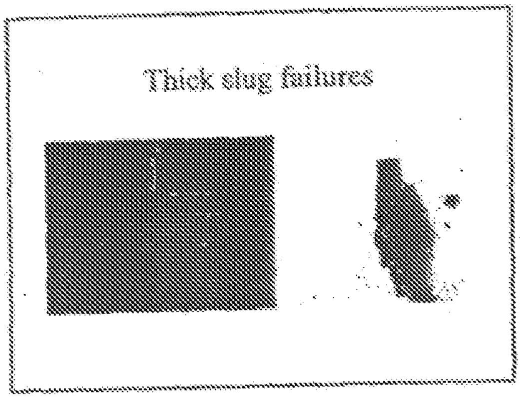
Recorded by: [signature]

Project No. [illegible]

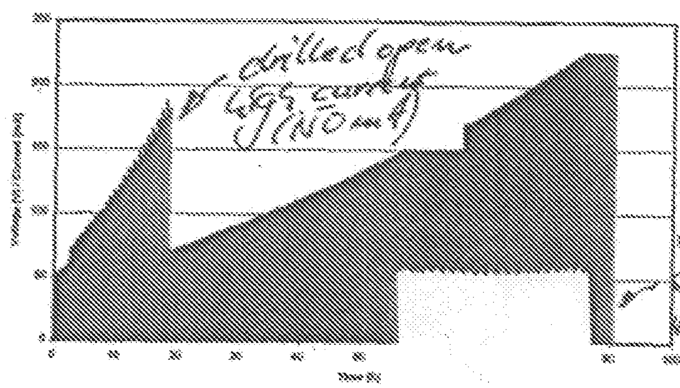
TITLE Anode slug processing [illegible] Book No. [illegible]

From Page No. 90

the occurrence of the failure modes I have observed before, when I anodized slugs of the same thickness (3 mm) in the same electrolyte with the same pulsed DC formation protocol.



This alone is a big improvement. I am now able to consistently form anodes of higher thickness (> 3 mm). In addition, the formation speed can be much, i.e., the current through the slug can be as high as 150 mA even 220 V without the occurrence of damage.



The graph on the right documents this; plotted is formation voltage over time; the drilled open structure allows much hig

To Page No. [illegible]

Witnessed & Understood by me, [signature] (35804)

Invented by [signature]

Recorded by [signature]

TITLE Anode processing idea Project No. P0149 Book No. 10210

From Page No. 91

currents and much faster formation times. The reason for the improved performance is probably improved convection, i.e. hot electrolyte can more easily come out of the structure and fresh electrolyte can be more readily flushed through the anode structure. I have started this work about 10 days ago and I have made now four drilled open thick anodes (8 mm) from various powders. I took two of the drilled open anodes and one un-drilled one and worked them into a real capacitor, the results of this work will be described on the following pages. I presented (to Schmidt, MEC) this material and the following results in todays seminar.

To Page No.

Witnessed & Understood by me, [signature] 35304

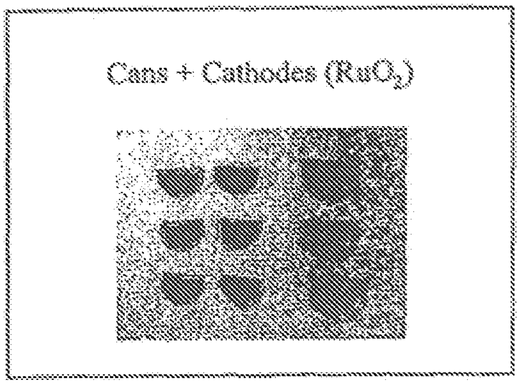
Invented by [signature]

Recorded by [signature]

From Page No. 92

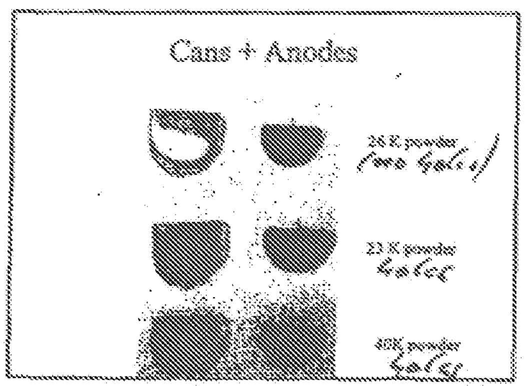
As indicated on page 92, three anode slugs were worked into a can with an installed cathode and an electrolyte, in the following sequence:

1)



RuO_2 coated Ti foils from Aerovox was cut into shape and spot welded into the Δ21 Ti can (2 foils per can)

2)



The following anodes were chosen:

1). 26 K-CV powder, 5.0 g/cc, small slugs, 1400°C sinter, formed to 22V
2) NH 270 (23K powder), small slugs, 1400 °C, 5.9 g/cm, 1.0 cc formed to 22V
3) 40 K powder, 1400°C, 5.0 g/cc, 1.0 cc, formed to 18V

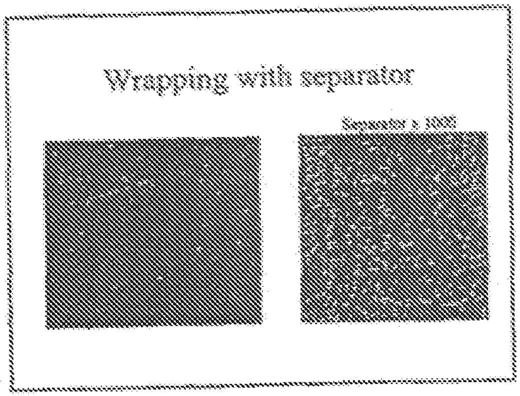
Witnessed & Understood by me, [signature] 3/30/

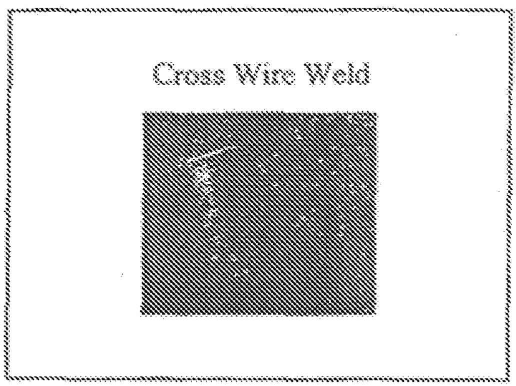
Invented by [signature]

Recorded by [signature]

TITLE Finished Zn cage in Δ21 can Project No. V0149 Book No. 10310

From Page No. 93





All three anodes were wrapped with GORE separator and taped for the [illegible] cages then they were inserted into the can with the spot-weld outside.

Then Kurt Lasky and I laser welded the top of the Δ21 can with the Ni feedthrough and the fill port onto the can after the Ni wire of the feed through was spot welded to the lead wire of the anode.

A procedure was necessary to turn off the [illegible] on the lead wire of the anode, then spot welding and laser welding proceeded smoothly.

The next step was to fill the can with electrolyte [illegible] following page.

To Page No. 95

Witnessed & Understood by me: [signature] (3530)

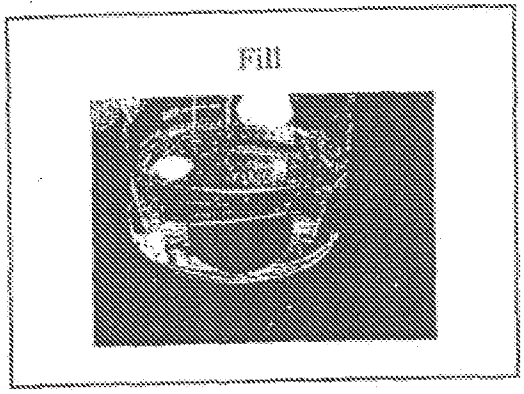
Invented by: [signature]

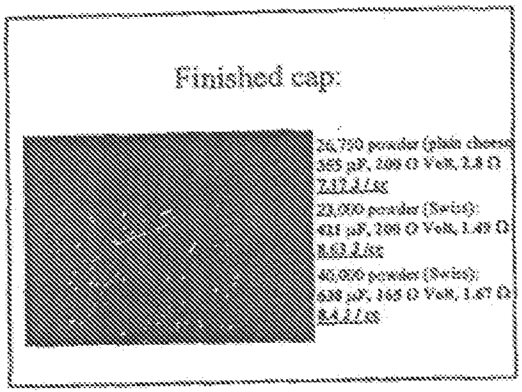
Recorded by: [signature]

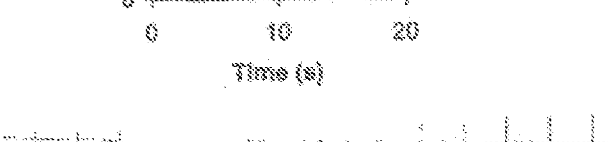
TITLE: Finished Ta caps

Project No. 60149
Book No. 10,210

From Page No. 94







A WGC recipe published in a ~~[illegible]~~ patent was used as the electrolyte. I filled by pumping the air out of a vessel which contained the unfilled capacitors.

After filling, I reformed the capacitors to the following working voltages:

26,750 powder: 200 Volts
23,000 powder: 200 Volts
40,000 powder: 165 Volts

The results are printed on the left and are encouraging.

Good charge times < 10 sec were achieved and the capacitors held charge at their working voltage.

To Page No. 96

Witnessed & Understood by me, [signature] 3520

Invented by [signature]

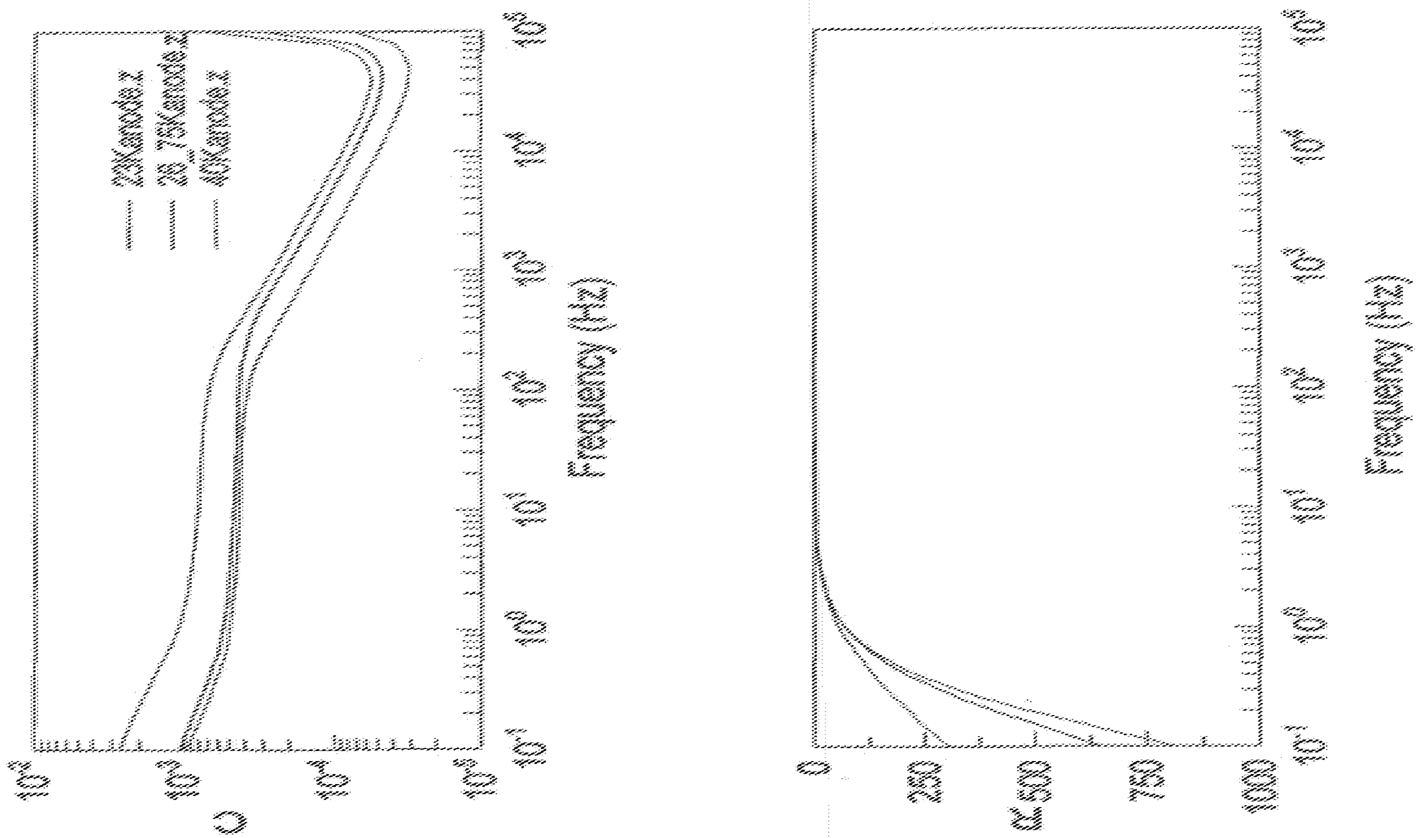
Recorded by [signature]

95A

Capacitance and Impedance Data of the Cgar [illegible] on pages 92-95

/

[illegible signature]



Project No. Vo149

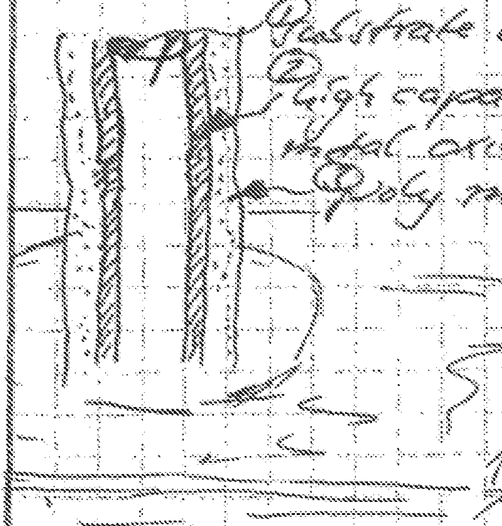
TITLE Anode precoating idea

Book No. 10210

From Page No.___

On pages 90-95, I have introduced the concept of drilling holes into the valve metal anode structure. During my talk in C. Schmidt's seminar on Dec. 21, I also mentioned that these holes may be filled with cathode wire. Here I will elaborate on this concept:

Holes or an array of holes in the anode, better, valve metal anode, will improve the ESR of the capacitor, as demonstrated in the experiment (page 95A). If cathode wire is inserted into the holes the ESR will even further improve. The cathode wire will be something like this:



To Page No. 100

Witnessed & Understood by me: 39304

Invented by

Date

Recorded by

continued from 100

101

would have to be joined by either cold welding or laser welding after they a stack

~~[illegible]~~

Using plates with the holes and inserting the cathode in the described way will reduce the ESR of the Al plate stack or the Ta/Nb center structure

witnessed and understood by me

Date: [illegible] ([illegible])

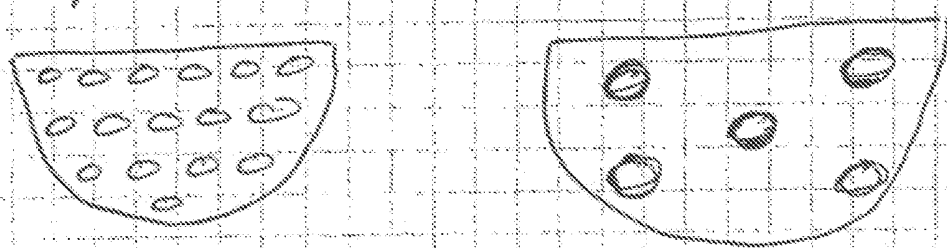
Invented by [illegible]

Recorded by [illegible]

From Page No. 99

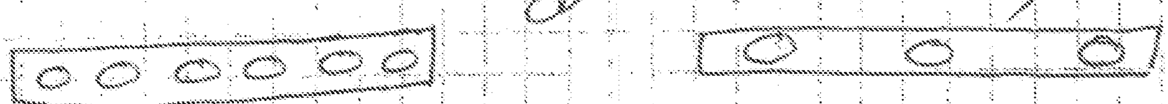
An array of holes with variable diameters may be introduced into the face or the side of a flat anode (see sketch):

top view. or less dense, but higher diameter top view



or

side view or side view (less dense)



The anode could consist of a sintered powder (e.g. Ta or Nb) or it could consist of stacked plates of Al, which have been previously formed.
In the Al case, inserting the cathode as rock will have the additional benefit of aligning the anode plates, according to a conversation with Steve Mag. In case of the Al plates, the plates

To Page No. 1?

are

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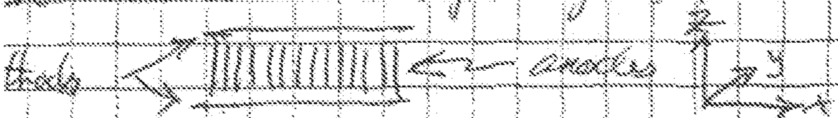
An aluminum electrolytic capacitor which uses a "slug" anode is currently under investigation. One method for creating the anode is to assemble a large number of long, thin strips of anode material into a "chewing gum package" arrangement, with cathodes on either side at right angles to the anode foil.



In this type of construction, current must flow parallel to the anode plates from the cathode before entering the etch tunnels of the anode plate which are parallel to the cathode plates. This results in a relatively high equivalent series resistance (ESR) for the capacitor.

Capacitor ESR may be reduced in several ways. One method is to place sheets of separator (very porous) paper between each anode plate or periodically. The drawback is that this introduces inert material into the capacitor and reduces volumetric efficiency.

Another method is to interplace sheets of lower capacitance very porous aluminum foil at periodic intervals in the anode stack. This can reduce ESR while not having as great an impact on volumetric efficiency.

Anode foils are typically mechanically worked prior to etching so the strip is on the (100) plane. An etching process is used to preferentially etch perpendicularly to the surface of the strip. Typically, "vertical" tunneling is encouraged and horizontal tunneling within the plane is to be avoided. In this situation, however, horizontal tunneling may be desirable as a connected network of horizontal tunnels will reduce the ESR of the capacitor.

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Alternatively, if the tunnel orientation can be changed to be perpendicular to the cathode foils, ESR may be greatly reduced. This could be accomplished by slicing the foil such that the foil is in the (011) plane of the material. Subsequent etching in the (100) direction would provide tunnels in the desired orientation. The use of a very thick foil sheet would be desirable in this situation.

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Project No. 72147

Book No. 8147

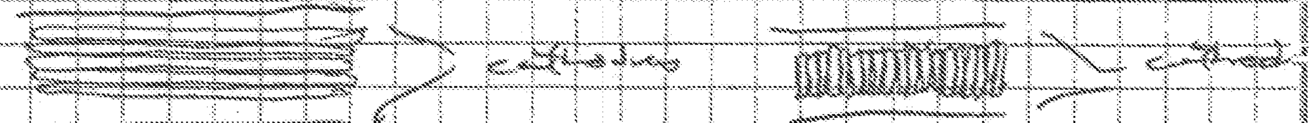
TITLE Capacitor with Sintered metal electrodes

From Page No.

Discussed on Pages 42 and 43 are methods for producing thin sintered metal electrodes with characteristics that reduce ESR and potentially increase energy density.

Using these thin foils, capacitors can be created with different electrode configurations. Typically, electrodes are pressed to form a thick slug. Access to the internal portion of these slugs becomes difficult as slug thickness increases. By creating a slug using thin foils as in (page 42) or modified (page 43) the surface increases access.

The proposed capacitors can be made by arranging plates either horizontally or vertically as shown below.



Horizontally layered electrodes

vertically layered electrodes.

In the horizontal case - green state modifications to lower ESR. In the vertical case electrode porosity is increased by defining plate spacing in green state surface roughness.

The capacitor can be made with a single anode or a plurality of anodes connected in parallel.

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From Page No. 3

On Page 40 of this Notebook, a method is described for making internal metal electrodes for capacitors using a tape casting process.

It is possible to modify these electrodes while they are in the "green tape" stage to reduce the resultant Equivalent Series Resistance (ESR) of the capacitor.

1) Roughen the tape surface.
   - This would provide regions of greater porosity between anode (or cathode) layers, where two "roughened" surfaces would meet.

2) Press channels, grids, arrays of channels, etc. into the green tape surface. When layers of electrodes are stacked, these channels will allow easy access for electrolyte to the internal regions of the stack.

3) Punch holes through the tape in the direction normal to its large planar surface. This may be done for single layers, prior to stacking, or after multilayer stacks.

4) Use a combination of the above techniques.

5) Other methods for increasing electrolyte access to the internal regions of the stack through modifying the green tape to provide channels, porosity.

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Karl Vitz

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